Lightweight cordierite–mullite refractories with low coefficients of thermal conductivity and high mechanical properties

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MS received 6 January 2014; revised 26 May 2014

Abstract. Lightweight cordierite–mullite refractories with low coefficients of thermal conductivity (CTCs), high strengths and high thermal-shock resistances were prepared using porous cordierite ceramics as aggregates. Phase compositions and microstructures of lightweight refractories were measured by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), etc. The effect of the relative mullite content of matrix (RMCM) on the microstructures and properties of lightweight refractories was investigated. It was found that the RMCM has a strong effect on the CTC and the mechanical properties. With an increase of RMCM, the compressive and flexural strengths of specimen increase. The thermal-shock resistance is the highest when the RMCM is 22 wt%, and also improved slightly when the RMCM is 46 wt% comparing with the specimen without mullite. When the RMCM is 46 wt%, the CTC reaches the minimum. Specimen with the RMCM of 46 wt% is the most appropriate mode, which has a moderate apparent porosity of 30%, a high compressive strength of 135.1 MPa, a high flexural strength of 20.5 MPa, a good thermal-shock resistance and a low CTC of 0.61 W mK^{-1} .

Keywords. Porous cordierite aggregate; lightweight refractories; microstructure; properties.

1. Introduction

Refractories are the essential materials for furnaces and the parts used at high temperature.¹ In recent times, with increased demand for saving energy and reducing CO₂ emission, more attention has been paid to lightweight refractories. Traditionally, lightweight refractories, fabricated by a conventional powder-processing route with the incorporation of some pore-forming agents, have a pore structure with large pore size and inhomogeneous pore size distribution, and then have low strengths and low thermal-shock resistances, which limited the application of traditionally lightweight refractories for working lining of high-temperature furnaces.²

Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) possesses a low thermal-expansion coefficient, an excellent thermal-shock resistance and chemical stability at elevated temperatures, and then the porous cordierite ceramics have attracted more attention.^{3–6} However, the porous cordierite ceramics are not suitable for the working lining of furnaces, because (1) the homogeneous microstructure of porous ceramics is harmful to the thermal-shock resistance; (2) the mechanical properties of cordierite material are poor. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has a low thermal-expansion coefficient and a good thermal-shock resistance as well as an excellent mechanical properties and a chemical stability. The relatively poor mechanical properties of cordierite ceramics can be improved by adding mullite as a reinforcing phase.^{7–9} Refractories, consisting of

aggregates and matrices, have inhomogeneous microstructures, although aggregates and matrices both have uniform microstructures. The inhomogeneous microstructures of refractories are beneficial to enhance the thermal-shock resistances.

Thus, introducing mullite into the matrices of the lightweight refractories containing porous cordierite ceramic aggregates, the lightweight refractories with high strengths and good thermal-shock resistances are expected to be obtained. But until now, the lightweight refractories containing porous cordierite aggregates have not been obtained, and the effect of mullite content of matrix on the microstructures and properties of the lightweight refractories has not been understood. These will be addressed in this work.

2. Experimental

Five lightweight refractories containing different mullite contents were prepared by using porous cordierite ceramics as aggregate and using cordierite powder, mullite powder, talc powder, corundum powder, α -Al₂O₃ micropowder, SiO₂ micropowder, ρ -Al₂O₃ powder, magnesia powder and calcium aluminate cement as matrix. Formulations of specimens are listed in table 1. The aggregates were prepared in our lab, and the microstructure of aggregate is shown in figure 1. The phase compositions of porous cordierite aggregate are major cordierite and minor spinel, the bulk density is 1.46 g cm^{-3} , the apparent porosity is 48%, the compressive strength is 5.3 MPa and the median pore size is $24 \text{ }\mu\text{m}$. The average

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Table 1. Formulations of specimens (wt%).

	A	B	C	D	E
Porous cordierite aggregate (0.088–5 μm)	50	50	50	50	50
Cordierite powder (<0.088 μm)	35	25	15	5	0
Mullite powder (<0.088 μm)	0	10	20	30	35
Talc powder (<0.088 μm)	2.5	2.5	2.5	2.5	0
Corundum powder (<0.088 μm)	0	0	0	0	3.3
$\alpha\text{-Al}_2\text{O}_3$ micropowder (APS = 3.64 μm)	2.4	2.4	2.4	2.4	4
SiO_2 micropowder (APS = 0.23 μm)	5.3	5.3	5.3	5.3	3.7
$\rho\text{-Al}_2\text{O}_3$ powder (<0.088 μm)	2	2	2	2	2
Magnesia powder (<0.088 μm)	0.8	0.8	0.8	0.8	0
Calcium aluminate cement (<0.088 μm)	2	2	2	2	2

Abbreviation: APS=average particle size.

Figure 1. Microstructure of porous cordierite aggregate.

particle sizes (APSs) of $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 micropowders were 3.64 and 0.23 μm , respectively.

Five lightweight refractories were named as A, B, C, D and E as listed in table 1. The rectangle parallelepiped specimens with the size of 125 mm length $\times$ 25 mm width $\times$ 25 mm thickness were casted for the porosity, density and strength measurement. The disc specimens with the size of 180 mm diameter $\times$ 20 mm height were casted for the testing of coefficient of thermal conductivity (CTC) according to the Chinese Standard YB/T 4130-2005. The specimens were cured for 24 h at room temperature, dried at 110°C for 24 h. Later the specimens were heated at 1360°C for 180 min in an electric furnace.

The apparent porosities were detected by Archimedes' Principle with water as medium. The compressive and flexural strengths of sintered specimens were measured at room temperature. The average particle size was measured by a laser particle size analyzer (Matersizer 2000). The phase analysis was carried out by an X-ray diffractometer (Philips Xpert TMP) with a scanning speed of 2° min⁻¹. The

relative contents of phases in the sintered specimens were evaluated using the standard-free quantitative method which has been used by Li *et al.*¹⁰ The pore size distribution and median pore size were obtained by a microscopy measurement method¹¹ through an optical microscope (Axioskop40). The microstructure of porous cordierite aggregate was observed by a scanning electron microscope (SEM) (Philips XL30) in the early research work, whereas, the microstructures of matrices were observed by a SEM (Philip, Nova Nano SEM 400, FEI) in the present work. The compositions of matrices were determined by calibration with EDAX ZAF quantification (standardless).

For the measurement of the flexural strengths after thermal shocks, the sintered specimens were inserted into a pre-heated furnace at 950°C, and then were held there for 25 min before they were quenched into a water container which was maintained at 25°C. Thermal shocks were repeated (total 3 cycles). After three thermal shocks, the flexural strengths of the quenched specimens were measured at room temperature. The residual strength ratio was obtained through the

flexural strength after thermal shocks/the flexural strength before thermal shocks $\times 100\%$, which used to evaluate the thermal-shock resistance.

3. Results and discussion

3.1 Phase composition, apparent porosity and bulk density

XRD patterns of specimens sintered at 1360°C are shown in figure 2 and the relative phase contents of specimens

Figure 2. XRD patterns of specimens.

Table 2. Relative phase contents of specimens (wt%).

	A	B	C	D	E
Cordierite	97	86	75	64	53
Mullite	0	11	23	32	44
Spinel	4	3	3	4	3
RMCM	0	22	46	64	88

Figure 3. Apparent porosities and bulk densities of specimens.

are listed in table 2. In specimen A, the phases are major cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, JCPDS # 01-084-1219) and minor spinel (MgAl_2O_4 , JCPDS # 96-900-3480); in other specimens, the phases are: major cordierite, major mullite ($\text{Al}_{4.50}\text{Si}_{1.50}\text{O}_{9.74}$, JCPDS # 96-900-1568) and minor spinel. From specimen A to specimen E, the relative mullite content of matrix (RMCM) increases gradually. In all specimens, spinels are mainly from the porous aggregates.

The influence of the RMCM on the apparent porosities and bulk densities of specimens are shown in figure 3. It can be seen, when the RMCM increases from 0 to 64 wt%, the apparent porosities and bulk densities change little, are 29–31% and $1.80\text{--}1.88\text{ g cm}^{-3}$, respectively. With a further increase of RMCM to 88 wt%, the apparent porosity decreases to 24%, and the bulk density increases to 2.08 g cm^{-3} . The change of apparent porosity may relate to the packing behaviour of particles. Specimens A to D have similar particle packing behaviour because of their similar particle size distributions (table 1), whereas, for specimen E, the decrease of SiO_2 micropowder ($\text{APS} = 0.23\text{ }\mu\text{m}$)

Figure 4. Compressive and flexural strengths of specimens.

Figure 5. Flexural strengths and residual strength ratios of specimens after thermal shocks.

content and the increase of α - Al_2O_3 micropowder ($\text{APS} = 3.64 \mu\text{m}$) content may make that the smaller particles fit into the pores between the larger particles more efficiently, and then increase the densities of the green and sintered specimens.

Usually, the refractories with porosity $\geq 30\%$ belongs to the lightweight refractories.^{11,12} In the present work, the measurement error of apparent porosity is 1%, and thus specimens A to D are lightweight refractories.

3.2 Strength, thermal-shock resistance and thermal conductivity

The influence of the RMCM on the compressive and flexural strengths of specimens is shown in figure 4. With an increase of RMCM, the compressive and flexural strengths increase remarkably. When the RMCM is 46 wt%, specimen C has a high compressive strength of 138.1 MPa and a high flexural strength of 20.5 MPa, which are much higher than those of

Figure 6. Coefficients of thermal conductivity of specimens at 500°C.

Figure 8. Pore size distributions of matrices in specimens.

Figure 7. Interface between aggregate and matrix in specimen C.

specimen A (RMCM is 0 wt%). When the RMCM is 88 wt%, the strengths reach to the maximum.

The influence of the RMCM on the flexural strengths and residual strength ratios of specimens after thermal shocks are shown in figure 5. The thermal-shock resistance of specimen

A without mullite is slightly higher than those of specimens D (RMCM is 64 wt%) and E (RMCM is 88 wt%), but slightly lower than that of specimen C (RMCM is 46 wt%). The thermal-shock resistance of specimen B (RMCM is 22 wt%) is the best, because the flexural strength and the residual

Figure 9. Microstructures of specimens A and E.

strength ratios both reach the highest value. It means that an appropriate RMCM could increase the thermal-shock resistance of lightweight refractory containing porous cordierite aggregates.

The influence of the RMCM on the CTCs of specimens at 500°C is given in figure 6. When the RMCM is 0, the CTC of specimen A is 0.70 W mK⁻¹. With an increase of RMCM, the CTC decreases gradually. The CTC reaches minimum (0.61 W mK⁻¹), when the RMCM is 46 wt%. Further increase of RMCM, increases the CTC substantially.

3.3 Discussion

Obviously, lightweight cordierite–mullite refractories with low CTCs, high strengths and high thermal-shock resistances have been obtained. Considering the strength and the CTC, specimen C (RMCM is 46 wt%) is the most apposite mode, which has an moderate apparent porosity of 30%, a high compressive strength of 135.1 MPa, a high flexural strength of 20.5 MPa, a good thermal-shock resistance and a low CTC of 0.61 W mK⁻¹. Although specimen C possess a lower apparent porosity of 30% compared to porous cordierite ceramics¹³ of 40% apparent porosity, the CTC and mechanical properties of specimen C are superior to those of porous cordierite ceramics.

Although the strength of the porous aggregate is low, the five castable refractories all have higher mechanical properties, even comparing with the dense refractory. It is because of their perfect bonding interfaces between matrices and aggregates, as shown in figure 7. In traditional dense refractories, the surfaces of dense aggregates are relatively smooth, and many microcracks exist at the interface between matrix and aggregate, which would decrease the strength; whereas, in the lightweight refractories, the surfaces of porous aggregates are rough, and no microcracks exist at the interface, which promote the formation of the perfect bonding interface (figure 7) and increase the strength of the lightweight refractories.

The differences of the properties of the five castable refractories come from their matrices, because they have the same porous aggregates. With an increase of RMCM, the strength and the CTC should be increased in theory, because the strength and CTC of mullite are higher than those of cordierite.^{9,11,14} However, with an increase of RMCM, the CTC decreases firstly, and reaches to the minimum CTC of 0.61 W mK⁻¹ when the RMCM is 46%, which relates to the microstructures of the matrices.

Pore size distributions of the matrices of specimens are shown in figure 8. Mono-modal pore size distributions are observed in the specimens A, D and E, and three-modal pore size distribution is observed in the specimen C. With an increase of RMCM, from specimen A to E, the peaks shift toward left largely. The median pore sizes of specimens A, C, D and E are 96, 60, 46 and 29 μm, respectively. In order to investigate the change of the pore distribution, the

microstructures of matrices of specimens A and E are given in figure 9. The pores are distributed homogeneously in the matrices of specimens, but the microstructures are rather different. In the matrix of specimen A, the big pores are a lot, the small pores are a few; in the matrix of specimen E, there are a lot small pores but a few big pores. It is clear that the results of the microstructures in figure 9 are mostly in accordance with those of the pore size distributions in figure 8. Simultaneously, the area of pore in matrix A is obviously bigger than that of matrix E, which is the further evidence that the apparent porosity of specimen A is bigger than that of specimen E. The decrease of pore size and the densification of matrix are helpful in improving the mechanical properties of specimens.

With an increase of RMCM, firstly, the mullite in matrix of specimen increases the CTC of specimen; secondly, the decreasing pore size of matrix decreases the CTC; and finally, the apparent porosity also affects the CTC, from specimen A to specimen D, the apparent porosity changes little, but the sharp decrease of the apparent porosity of specimen E increases the CTC; when the RMCM is 46%, the balance is reached among the three aspects, which is the main reason why specimen C has the lowest CTC.

4. Conclusions

Lightweight cordierite–mullite refractories with low CTCs, high strengths and high thermal-shock resistances have been obtained. The RMCM has a strong effect on the CTC and the mechanical properties. The detailed results are as follows:

- (1) With an increase of RMCM, the compressive and flexural strengths of specimen increase. The thermal-shock resistance is the highest when the RMCM is 22 wt%, and also improved slightly when the RMCM is 46 wt% comparing with the specimen without mullite.
- (2) When the RMCM is 46 wt%, the CTC reaches the minimum, because the balance is reached among the effects of the RMCM, the average pore size and the apparent porosity.
- (3) Specimen with the RMCM of 46 wt% is the most apposite mode, which has a moderate apparent porosity of 30%, a high compressive strength of 135.1 MPa, a high flexural strength of 20.5 MPa, a good thermal-shock resistance and a low CTC of 0.61 W mK⁻¹.

Acknowledgements

We like to thank the Natural Science Foundation of Hubei Province (no. 2011CDB238) and the 973 Program earlier research project (no. 2012CB722702) for financially supporting this work.

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